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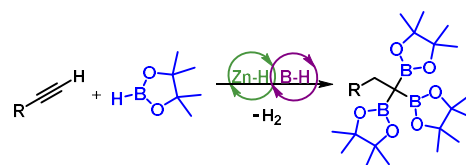


A comparison of two zinc-hydride catalysts for terminal alkyne C-H borylation/hydroboration and the formation of 1,1,1-triborylalkanes by tandem catalysis using Zn-H and B-H compounds

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ABSTRACT: The synthesis of 1,1,1-triborylalkanes from terminal alkynes and pinacolborane (HBPin) is reported. This transformation proceeds via initial Zn-catalyzed alkyne C-H borylation, which can be achieved using a NacNacZnH complex. Combinations of a NacNacZn-alkynyl formed via C-H zincation of a terminal alkyne and HBPin exist in equilibrium with the alkynyl-BPin and NacNacZnH. The consumption of NacNacZnH by irreversible reaction with a terminal alkyne evolving H₂ is essential for driving alkyne C-H borylation to completion. The alkynyl-BPin compounds undergo hydroboration catalyzed by Zn-H complexes at raised temperatures with a {7DIPP}ZnH(NTf₂) complex (7DIPP = 1,3-bis(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-1H-1,3-diazepin-3-ium-2-ide) a more active catalyst for hydroboration than a NacNacZnH complex. Calculations indicate the {7DIPP}Zn-H congener has more pronounced biphilic character than NacNacZnH (greater electrophilicity at Zn while maintaining a sufficiently basic hydride). Of the two hydroboration steps, the hydroboration of alkynylBPin is catalyzed by Zn-H complexes, whilst the hydroboration of 1,1-diborylalkenes is catalyzed more effectively by B-H containing species, including boranes formed in-situ from HBPin. These observations led to a one-pot protocol being developed for converting terminal alkynes into 1,1,1-triborylalkanes that utilizes {7DIPP}ZnPh(NTf₂) as a precatalyst for the formation of 1,1-diborylated alkenes with subsequent addition of BH₃-THF as catalyst for the final step.

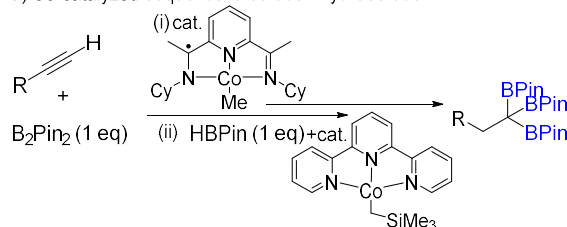


Introduction

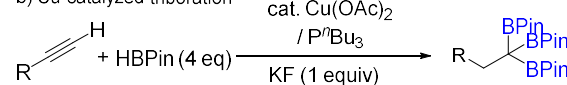
Organoboron compounds have become staple reagents in chemical synthesis as they possess a desirable balance between stability and facile transformation into other functional groups.¹ Multiply borylated organic compounds embody especially attractive reagents because of the potential for the stepwise, selective conversion of the boryl groups into C-C and C-heteroatom bonds.² While compounds such as geminal bisborylalkanes have been extensively utilized in synthetic endeavours,³ 1,1,1-triborylalkanes have received much less attention. This is partly due to the greater complexity of making these compounds selectively and efficiently, a challenge that only recently has begun to be addressed. While the first selective route to 1,1,1-triborylalkanes is over 40 years old this multiple boronation of alkyl halides required excess lithium metal.⁴ Recently, more efficient routes to 1,1,1-triborylalkanes have been achieved using transition metal catalysis. For example, Ir-catalyzed C(sp³)-H triborylation of 2-ethylpyridines,⁵ and Ni-catalyzed triborylation of benzylic C-H bonds.⁶ Styrenes are also effective precursors to 1,1,1-triborylalkanes via Co-catalyzed borylation/hydroboration of vinylarenes,⁷ and Rh-catalyzed borylation/hydroboration of (*E*)-styrylboronates.⁸ Nonetheless, general routes to 1,1,1-triborylalkanes using simple hydrocarbon starting materials and inexpensive, low toxicity earth abundant metal based catalysts are desirable for the wider uptake of these compounds in synthesis.

Previous work on terminal alkyne multi-borylation:

a) Co-catalyzed sequential diboration/hydroboration



b) Cu-catalyzed triboration



c) Zn-catalyzed borylation/hydroboration

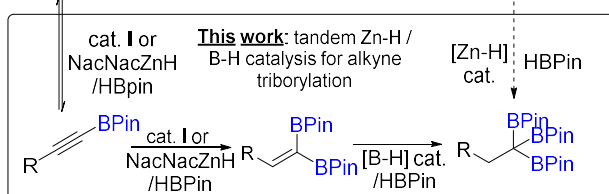
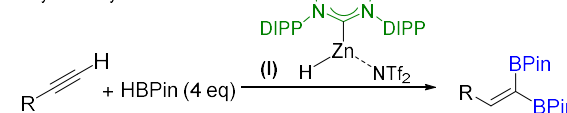


Figure 1: Select previous work, inset this work on tandem Zn-H / B-H catalysis for forming 1,1,1-triborylated alkanes.

Terminal alkynes are attractive precursors to 1,1,1-triborylated alkanes as they are readily available inexpensive feedstocks. In this area, Chirik et al. utilized two different cobalt catalysts (Figure 1, top) to afford triborylated alkanes by firstly performing the 1,1-diboration of terminal alkynes with bis(pinacolato)diboron (B_2Pin_2) followed by hydroboration with pinacolborane (HBPin).⁹ While notable work, cobalt has low permitted daily exposure (PDE) limits thus catalysts based on earth abundant 3d metals with much less stringent PDE values, such as Fe, Cu or Zn, would be preferable.¹⁰ During the course of this study, Marder et al. reported a Cu-based catalyst capable of the 1,1,1-triborylation of terminal alkynes in the presence of stoichiometric KF. This work (Figure 1b) represents a highly efficient method to access these compounds using a low toxicity and earth abundant metal based catalyst.¹¹

There is an increasing interest in using zinc complexes as borylation catalysts,¹² and recently we demonstrated that a NHC-Zn complex, $\{7DIPP\}ZnH(NTf_2)$ (**I**, Figure 1c) or its precursor, $\{7DIPP\}ZnPh(NTf_2)$ (**II**), are capable of catalyzing both the C-H borylation of terminal alkynes and the hydroboration of the alkynylBPIn product affording 1,1-diborylated alkenes. In this work the hydroboration step proceeded via alkyne hydrozincation then H-B / Zn-C metathesis.¹³ Experimental findings supported by DFT calculations revealed that **I** contains a highly electrophilic zinc center and a hydridic (thus Brønsted basic) Zn-H moiety, thus **I** is biphilic in character. Arguably the most well studied low coordinate zinc hydride complexes use the β -diketiminate ligand (NacNac), with a *N*-DIPP substituted NacNac derivative enabling formation of a three coordinate zinc hydride, termed herein (DIPPNacNac)ZnH, **III** (Scheme 1, DIPPNacNac = $\{2,6\text{-}iPr_2H_3C_6N(CH_3)C\}_2CH$).¹⁴ While **III** and other low coordinate zinc-hydrides have been reported to catalyze the hydrosilylation and hydroboration of ketones and aldehydes, as well as the hydrosilylation of CO_2 , **III** has not been used to catalyze alkyne borylation to the best of our knowledge.^{15, 16, 17} Herein we report our studies comparing the reactivity of the low coordinate zinc hydride complexes **I** and **III** in the borylation of terminal alkynes. This led to the development of a tandem Zn-H/B-H catalytic system for the one-pot transformation of terminal alkynes into 1,1,1-triborylalkanes.

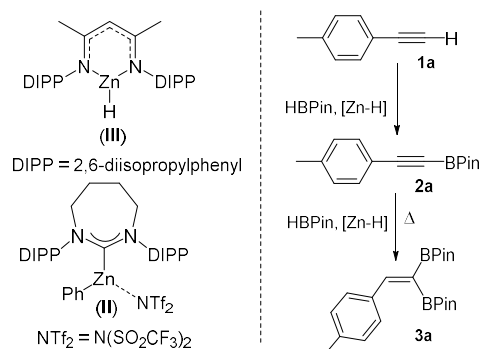
Results and Discussion

Comparison of the reactivity of Zn catalysts

The reported 1,1-diboration of 4-ethynyltoluene (**1a**, right Scheme 1) with HBPin catalyzed by **I** or **II** (as a more readily accessible precatalyst), required heating to 90 °C for significant conversion of the alkynylBPIn **2a** to **3a**.¹³ Compound **III** was explored to determine if it was a more active catalyst than **I** in this transformation. However, from multiple attempts using **III** to catalyze the formation of **3a** from alkyne **1a** it became evident that **III** is a less effective catalyst than **I/II** for this conversion. This is illustrated by there being no observable formation of **3a** (by multinuclear NMR spectroscopy) after 25 h at 90 °C using 10 mol% of **III** in C_6D_6 (in a sealed tube). In contrast, using **I** under identical conditions **3a** is formed in good yield (and up to 73 % yield after 36 h). Only when the reaction temperature is increased to 110 °C does **III** catalyze the formation of **3a** to any observable extent, albeit requiring 120 h at 110 °C to reach 90 % conversion of **2a** to **3a**.

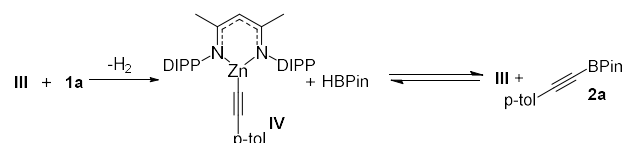
To explore the disparity between the two Zn-H catalysts the initial step, formation of **2a** by C-H borylation, was explored.

Comparing the activity of **III** to that of **I** for alkyne C-H borylation under identical conditions (1.1 equiv. of HBPin, 10 mol % catalyst, 1 M THF solution, 60 °C) after only 120 min, 98 % of **2a** was formed using **III**, making it faster than borylation catalyzed by **I**. However, if the reaction is performed in C_6D_6 **I** is slightly more active than **III** (though both are effective catalysts). We attribute this solvent disparity to the differing propensity of **I** and **III** to bind THF due to their relative electrophilicity (vide infra).



Scheme 1: The stepwise transformation of terminal alkynes into 1,1-diborylated alkenes using Zn-H **III** and precatalyst **II** (which forms **I** in-situ on metathesis with HBPin).

To gain further insight into the reactivity of **III**, stoichiometric reactions were performed. When **III** was reacted with terminal alkyne **1a** in a 1:1 ratio at room temperature in benzene, alkyne deprotonation takes place as evidenced by the consumption of the alkynyl $C\equiv C-H$ resonance in the 1H NMR spectrum and concomitant formation of H_2 ($\delta_H = 4.47$ ppm). The reaction affords a single major new (DIPPNacNac)Zn containing product consistent with a (DIPPNacNac)Zn(alkynyl) species (**IV**, Scheme 2).¹⁸ The subsequent addition of one equivalent of HBPin to **IV** resulted in formation of **2a**, as indicated by growth of a diagnostic resonance at 24.9 ppm in the ^{11}B NMR spectrum, and **III** concomitantly (indicated by the growth of the diagnostic Zn-H resonance at 4.37 ppm in the 1H NMR spectrum). However, despite Zn- C_{sp} / H-BPin metathesis taking place at room temperature, this transformation does not go to completion (after 24 h at room temperature). This is not due to kinetic factors as after prolonged heating and then cooling back to room temperature the same ratio of **IV**: **2a** was observed, indicating an equilibrium process. As the equilibrium position was reached at room temperature Zn-C / H-B metathesis proceeds with a relatively low barrier for this system. Consistent with this, combining **III** and **2a** in benzene led to a mixture containing **III**, **2a** and the metathesis products HBPin and **IV** at room temperature confirming reversibility. This is comparable to previously reported reactivity observed on combining complex **I** with alkynylBPIn species (where a σ -bond metathesis equilibrium was also observed). This suggests that reversible metathesis between Zn-H and (sp) $C-B$ compounds with ΔG close to zero may be a common phenomenon for low coordinate zinc complexes.



Scheme 2: The deprotonation of alkyne **1a** by **III** and reversible σ -bond metathesis between **IV** and HBPin.

To further assess the relative reactivity of {7DIPP}Zn and NacNacZn systems calculations at the M06-2x/lanl2dz/6-311G/PCM(THF) level were performed. For the NacNacZn system while alkyne deprotonation is thermodynamically favored (equation 1) the metathesis of the resultant zinc-alkynyl species with HBPIn is energetically uphill (equation 2), albeit by < 2 kcal/mol⁻¹. Thus the subsequent reaction of **III** with further terminal alkyne is key to drive the reaction to completion and thus ensure high conversions of the alkynylBPIn. Again this is comparable with observations previously reported for the {7DIPP}Zn congener (see Figure 2 inset).

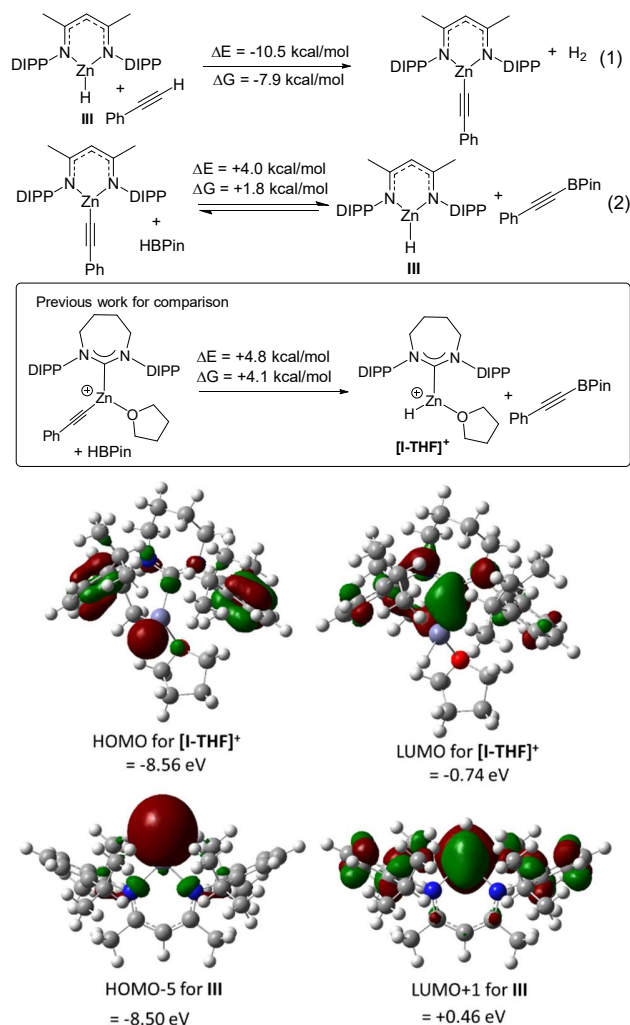


Figure 2: Top, the calculated energy changes for C-H zincation and for Zn-C / H-BPin metathesis for NacNacZn complexes and inset for comparison for NHC-Zn complexes.¹³ Bottom, comparison of key select frontier molecular orbitals of **III** and **[I-THF]⁺** at isosurface value = 0.04.

Comparison of the frontier molecular orbitals of **[I-THF]⁺** (see footnote)¹⁹ and **III** indicated that as expected **[I-THF]⁺** is more electrophilic than **III**. The LUMO of **[I-THF]⁺** (Figure 2) has significant zinc character and at -0.74 eV is significantly lower in energy than the LUMO+1 of **III** (+0.46 eV) (the LUMO for **III** has no zinc contribution). However, the energy of the highest occupied molecular orbital with significant Zn-H character is comparable for both, for **[I-THF]⁺** it is the HOMO (-8.56 eV)

and for **III** it is the HOMO-5 (-8.50 eV). Also notably, comparison of the NBO charges of the Zn-H moiety in **[I-THF]⁺** and in **III** found that the hydride in **[I-THF]⁺** has comparable magnitude of negative charge to that of the hydride in **III** (-0.544 and -0.460, respectively). The positive charge on Zn is also comparable in **[I-THF]⁺** and in **III** (+1.155 and +1.104, respectively). The energy of the key frontier orbitals and the charge distribution both support the hypothesis that low coordinate {7DIPP}Zn-H cations combine considerable electrophilicity at zinc with a hydridic moiety. The more pronounced biphilic character (due to the lower LUMO energy) is possibly the key to the superior catalytic performance of **I** relative to **III**.

Formation of 1,1,1-triborylated alkanes

During the comparison of **I** and **III** in alkyne borylation varying quantities of the 1,1,1-triborylated alkane **4a** were observed at raised temperatures when using **I** (or **II**, e.g. Table 1, entries 1-3). No significant amount (< 5%) of **4a** was observed in any reaction using **III** as the catalyst (even after 160 h at 110°C in a sealed tube). Using precatalyst **II**, changing the solvent to other arenes such as toluene, did not affect the outcome of this transformation significantly (entry 3 vs 4). Therefore C₆D₆ was used purely to facilitate in-situ reaction monitoring. Decreasing the catalyst loading had a detrimental effect while increasing the concentration helped to increase the yield (Table 1, entries 6-7). Despite some improvements, reactions required long times at high temperature to form significant **4a** and unreacted diborylated alkene **3a** was observed in these reactions indicating incomplete conversion even after 24 h.

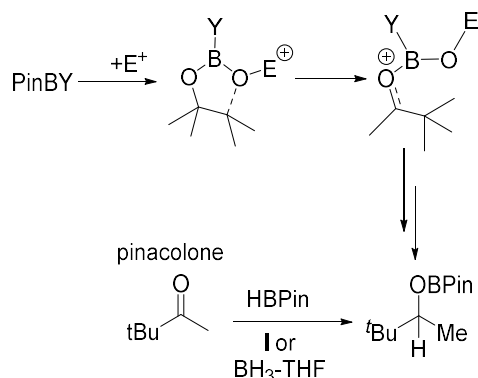
Table 1. Optimization for synthesis of 1,1,1-triborylalkane^a

Entry	T (°C)	Conc [mol/l] ^e	Time [h]	4a ^f
1 ^b	90	1	36	<1%
2	100	1	24	<5%
3	110	1	24	40
4 ^c	110	1	24	46
5 ^d	110	1	96	56
6	110	2	24	48
7	110	3	24	70

^a Reaction conditions as shown unless otherwise indicated. ^bUsing 4 eq of HBPIn, previous work (ref 13). ^cUsing toluene instead of benzene. ^dUsing 5 mol % of **I**. ^eRefers to the concentration of terminal alkyne **1a**. ^fYields determined by in-situ ¹H NMR spectroscopy vs CH₂Br₂ as an internal standard.

During reactions using **I** or **II** significant HBPIn decomposition was observed, with growth in ¹¹B resonances observed between 20-22 ppm consistent with (RO)₃B species. Concomitantly, new H-B containing species were observed (as indicated by multiplets with ¹J_{B-H} couplings, including at -13 and -40 ppm in ¹¹B NMR spectra). It is feasible that under forcing conditions NHC dissociation from Zn is occurring,¹³ and this Lewis base may facilitate degradation of HBPIn.²⁰ However, an alternative de-

composition pathway is also proceeding as indicated by formation of 2,2-dimethyl-3-OBPin-butane (Scheme 3), indicated by a diagnostic resonance at 3.95 ppm (q, $^3J_{\text{HH}} = 6.3$ Hz).²¹ This is presumably formed by electrophilic activation of a BPin species inducing a pinacol rearrangement (methyl migration, see Scheme 3) with subsequent hydroboration yielding the observed product, 2,2-dimethyl-3-OBPin-butane. Indeed, pinacolone was hydroborated to this product using HBPIn under the reaction conditions catalyzed by **I** or $\text{BH}_3\cdot\text{THF}$ (Scheme 3).



Scheme 3: Electrophile (E^+) initiated formation of 2,2-dimethyl-3-OBPin-butane.

The extensive HBPIn degradation observed in the presence of **I/II** at raised temperatures suggested that B-H species effective for catalyzing hydroboration may be formed in-situ.²² Analysis of the decomposition of HBPIn during catalysis using precatalyst **II** at 60, 90 and 110°C (see Supporting Information) revealed that although formation of $(\text{RO})_3\text{B}$ species and 2,2-dimethyl-3-OBPin-butane is observed at all three temperatures, it takes much longer at the two lower temperatures. The same analysis also showed that the formation of **4a** (monitored using the characteristic ArCH_2 resonance at 3.19 ppm) has an induction period (despite significant **3a** being present in solution after short reaction times at 110°C). Together these observations suggested in-situ formation of a B-H species that acts as a catalyst enabling formation of the triborylated alkane **4a**. This borane is presumably formed by reaction of a $\{7\text{DIPP}\}\text{Zn}$ species with HBPIn as minimal HBPIn degradation was observed in reactions using **III** under identical conditions. Thus the disparity between the reactions using **I** and **III** is attributed to the absence of an in-situ formed B-H catalyst²³ in reactions using $(\text{DIPPNaCNac})\text{Zn}$ species due to the lower Lewis acidity of **III** relative to **I** (and derivatives).

Hydroboration of 1,1-diborylalkenes by B-H containing species

While $\text{THF}\cdot\text{BH}_3$ was previously shown to be poor at catalysing hydroboration of alkynylBPin **2a** to **3a** (particularly relative to **I**), we surmised that the increased steric bulk present in the 1,1-diborylalkene **3a** afforded by the two BPin units may significantly disfavour hydrozincation of **3a** with sterically encumbered $(7\text{-DIPP})\text{Zn}\cdot\text{H}$ species. Therefore the ability of some common boranes to effect hydroboration of the 1,1-diborylated alkene **3a** to **4a** was explored (Table 2).

Table 2. Hydroboration of 1,1-diborylalkene **3a** using borane catalysts^a

Entry	BH-cat	T (°C)	concentration	Time / h	4a ^c
1	BEt_3	110	3 M	24	37
2	$\text{BH}_3\cdot\text{SMe}_2$	110	3 M	5	52
3 ^b	$\text{BH}_3\cdot\text{SMe}_2$	110	3 M	24	20
4	$\text{BH}_3\cdot\text{THF}$	110	3 M	5	79
5	-	110	3 M	24	70

^aReaction conditions as shown unless otherwise indicated. ^b BH_3SMe_2 added after alkynylBPin (**2a**) formation instead of after formation of **3a**. ^cYields determined by in-situ ^1H NMR spectroscopy based on the ratio of product vs CH_2Br_2 added after the time shown as an internal standard.

BEt_3 was initially explored as it reacts in aromatic solvents with HBPIn to form H_yBEt_x ($x + y = 3$) species, and we surmised that low steric bulk, base free $\text{R}_2\text{BH}/\text{RBH}_2$ species may be required for catalyzing hydroboration of bulky **3a** via a mechanism related to that recently identified.²⁴ Sub-stoichiometric amounts of BEt_3 were added to the standard reaction mixture (which still contains excess HBPIn) after the formation of diborylated alkene **3a** using **I** (or **II**). This led to formation of EtBPIn , H_yBEt_x ($x + y = 3$) species (by ^{11}B NMR spectroscopy) and the desired product **4a**, albeit in modest yield (Table 2, entry 1). Next, guided by the work of Thomas, Cowley and co-workers,²² BH_3 compounds were explored and found to be more effective catalysts (entry 2). However, if BH_3 species were added earlier, specifically after formation of the alkynylBPin **2a** under otherwise identical conditions lower yields of 1,1,1-triborylalkane **4a** were obtained (compare entries 2 and 3). This is consistent with the importance of a Zn-H in efficiently forming the diborylated alkene (**3a**) as previously discussed.¹³ $\text{BH}_3\cdot\text{THF}$ proved the most effective catalyst when added post formation of the 1,1-diborylalkene (formed using **I** or **II**) with 10 mol% $\text{BH}_3\cdot\text{THF}$ affording the desired product **4a** in much shorter reaction times and with higher yields than using just **I** or **II** (entry 4 vs 5).

With effective conditions for the synthesis of 1,1,1-triborylated alkanes (**4x**) from terminal alkynes identified using combined Zn-H / B-H catalysts, triborylation of a range of terminal alkynes was investigated. The substrates selected was determined by our previous report which documents the functional groups tolerated by species **I/II**.¹³ Aromatic alkynes with both electron-donating and electron-withdrawing substituents were amenable providing the desired products **4x** in moderate to good yields (Figure 3). It should be noted that electron-withdrawing substituents required slightly longer reaction times in the Zn catalyzed transformation of terminal alkynes to diborylated alkenes consistent with our previous report.¹³ Haloaryl-substituted alkynes were also tolerated and no C-X ($\text{X} = \text{Br}, \text{Cl}, \text{F}$) bond cleavage was detected. Furthermore, heteroaromatic and polyaromatic substrates such as 3-ethynylthiophene or 1-ethynyl-naphthalene were suitable substrates for this methodology. However, in the case of 3-ethynylthiophene, despite prolonged heating only 30% of **4j** was obtained with significant amount of the 1,1-diborylalkene **3j** remaining unreacted. Thus the BH_3 -catalyzed

hydroboration is not efficient with this substrate. Furthermore, 1-ethynyl cyclohexene did not react to produce any significant amount (< 10 %) of triborylated product. It should be noted that for several of substrates in Figure 3 omission of BH₃-THF was tested in the final step but this led to lower yields of **4x** in all cases under otherwise identical conditions.

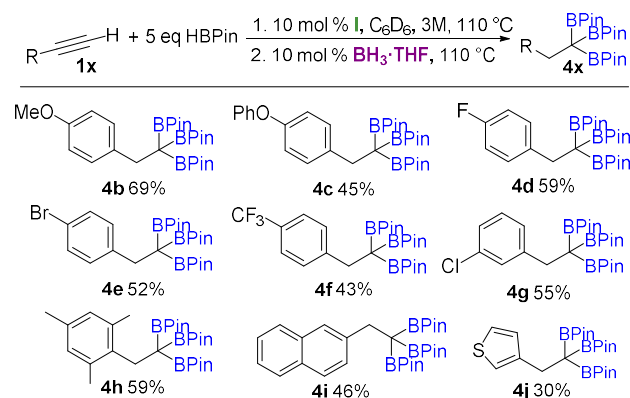
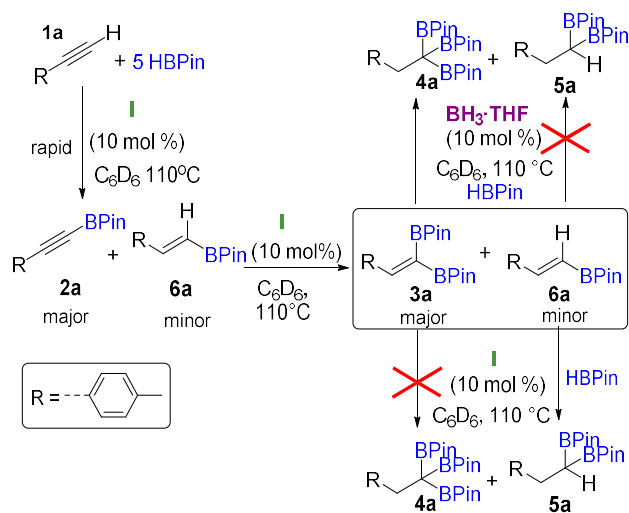


Figure 3. Scope of tandem Zn-H / B-H catalyzed triborylation of terminal alkynes. Yields by in-situ ¹H NMR spectroscopy vs CH₂Br₂ as internal standard.

The mass balance in these reactions was composed largely of a second borylated alkane product, **5x**, indicated by a diagnostic doublet (³J_{HH} ≈ 8 Hz) at *ca.* 2.7–2.9 ppm in the ¹H NMR spectra, consistent with a 1,1-diborylated alkane. The formation of **5x** (Scheme 4) is presumably via double hydroboration of the terminal alkyne as the 1,1,1-triborylated alkanes are stable under these reaction conditions (i.e. do not undergo protodeboronation in-situ). It was previously shown that in aromatic solvents while dehydrogenative borylation of **1x** to form **2x** dominates using **I** or **II** minor quantities of hydroboration products, e.g. 2-[(E)-2-p-tolylenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**) are observed.¹³ In-situ analysis of the reaction starting from **1a** under standard conditions (110 °C, 3 M benzene solution, 5 equivalents HBPIn, 10 mol% of **II**, sealed tube) revealed formation and then consumption of the E-styrylboronate **6a**. Compound **6a** has an indicative resonance at 6.10 ppm (d, ³J_{HH} = 18.3 Hz) that is replaced by the appearance of a new doublet as the reaction proceeds at 2.87 ppm (³J_{HH} = 8.2 Hz) consistent with **5a**.

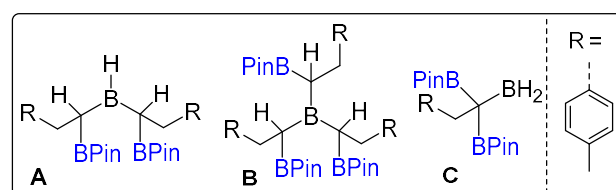
Identification of catalytically active species

To determine the catalytically active species for the formation of **4a** and **5a**, compounds **3a** and **6a** were prepared independently. Adding 10 mol% BH₃-THF to **3a** and HBPIn, led on heating (110°C, 5 h) to high yielding conversion to **4a**, confirming a zinc species is not required for this step. In contrast, attempting the BH₃-THF catalyzed hydroboration of **6a** afforded no detectable (by ¹H NMR spectroscopy) formation of **5a** (even at 110°C). In contrast compound **II** catalyzed production of **5a** from **6a** using HBPIn (61% yield after 15 h at 110 °C). Thus B-H species, such as BH₃-THF, are effective for the transformation of **3a** to **4a** but are ineffective for the transformation of **6a** to **5a**, with the opposite selectivity observed using **I**.



Scheme 4. The formation of **4a** and **5a** during terminal alkyne borylation/hydroboration catalyzed by Zn-H and B-H species.

It was hypothesized that the failure of BH₃-THF to effect catalytic hydroboration of **6a** with HBPIn is due to the reaction of BH₃-THF with multiple equivalents of **6a** to form sterically hindered compounds such as **A** / **B** (and isomers thereof, Scheme 5). Hindered R₃B compounds have been demonstrated to not undergo metathesis with HBPIn,²⁴ thus it is feasible that species like **A** or **B** would not react (or only react very slowly) with HBPIn even on heating. The reaction of BH₃-THF with two equivalents of **6a** in the absence of HBPIn at ambient temperature led to a complex mixture, but key observations include: the complete consumption of **6a**; the formation of alkylBpin species (indicated by δ_{11B} = 34.1 ppm); the persistence of some BH₃-THF. Furthermore, these products did not react further on addition of HBPIn and heating. This confirms a non-stoichiometric reaction occurs between **6a** and BH₃-THF to afford inactive (towards HBPIn metathesis) organoboranes.



Scheme 5: Possible products from the reaction of BH₃-THF with **6a** (**A** / **B** and isomers thereof) and **3a** (**C**) these compounds may also be THF adducts/ hydride bridged dimers of **A-C**.

The number of equivalents of an alkene BH₃ species react with is highly dependent on alkene steric bulk; for example Brown and co-workers showed that BH₃-THF and excess 2-methyl-2-butene proceeded rapidly to the dialkylborane product, while even with excess of the more bulky alkene 2,3-dimethyl-2-butene the reaction only proceeded to the monoalkylborane product.²⁵ Thus different alkene : BH₃-THF reaction ratios (and thus different degrees of sterics around boron and thus different barriers to metathesis with HBPIn) maybe the origin of the reactivity disparity between **3a** and **6a** with BH₃-THF. Consistent with this combining two equivalents of **3a** and BH₃-THF led to a rapid reaction, but incomplete consumption of **3a** (indicating a 1:1 reaction stoichiometry) and the formation of a

product consistent with **C**. On combination with HBPIn this reaction mixture yielded **4a** on heating. This indicates that the barrier to metathesis with HBPIn for species derived from **3a**/BH₃ (such as **C**) is significantly lower than that for species derived from **6a**/BH₃ (such as **A** / **B**). Thus the ability of BH₃ species to catalyze hydroboration using HBPIn is highly dependent on the steric bulk of the alkyne / alkene, which in turn controls the reaction stoichiometry between alkene/BH₃.

Conclusions

Direct comparison of {7DIPP}Zn(H)(NTf₂) (**I**) with a NacNacZnH (**III**) complex revealed that both can catalyze alkyne C-H borylation and alkyne hydroboration and that Zn-C(sp) / H-BPin metathesis was reversible for both. However, NacNacZnH (**III**) was a poorer catalyst for alkynylBPIn hydroboration. This is attributed to the greater biphilic character of {7DIPP}ZnH species, which are more electrophilic than the NacNacZn congeners (based on the energy of the key zinc based unoccupied orbital) while still being sufficiently hydridic. At raised temperatures {7DIPP}Zn species enabled the formation of 1,1,1-triborylated alkanes. However, this occurs after significant decomposition of HBPIn suggesting catalysis by in-situ formed B-H species is key for the hydroboration of 1,1-diborylated alkenes in this case. Adding 10 mol% BH₃-THF after 1,1-diborylalkene formation led to more rapid formation of 1,1,1-triborylated alkanes in higher yield. This serves as another reminder of the potential for “Trojan horse”²³ hydroboration catalysis when using boranes such as HBPIn. Notably, the ability of BH₃-THF to catalyze production of borylated alkanes by hydroboration / HBPIn metathesis was found to be highly dependent on the substituents of the alkene. In this work the bulkier alkene undergoes BH₃ catalyzed hydroboration with HBPIn, while a less bulky alkene did not. This was attributed to differences in the alkene:BH₃ reaction stoichiometry leading to different intermediates (R₂BH vs RBH₂) that have significantly different steric environments around boron thus different barriers to metathesis with HBPIn.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information listed below is available free of charge on the ACS Publications website at DOI:

Synthetic methods and characterization details (.PDF).
Computed Structures (.XYZ)

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